Proceedings of CONF-FMCE 2025 Symposium: Semantic Communication for Media Compression and Transmission
DOI: 10.54254/2755-2721/2025.GL28785

Nano-Structuring for Sodium-Ion Batteries: Hard Carbon and Prussian Blue Systems for Range and Conversion Efficiency

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Abstract. Sodium-ion batteries are considered low-cost sustainable replacement to lithium-ion batteries due to the abundance and low-cost of sodium, but its application has been limited by its low energy density. Recent studies have shown hard carbon anodes and Prussian blue analogue cathodes as promising in improving Sodium-ion batteries' energy density. Both materials are structurally ideal as they include open or porous structures for the transportation and intercalation of large sodium ions, leading to better electrochemical performance compared to traditional metal oxide and phosphate cathodes and graphite anodes. Both materials also exhibit high structural tunability, with hard carbon having adjustable ratio of graphitic and pore domain and Prussian blue analogues have substitutable redox sites. Recent studies also found that flash Joule heating of hard carbon will produce a metastable anode with increased capacity and controlling the interstitial water content in Prussian blue cathode can tune its capacity and longevity. This paper discusses recent research regarding hard carbon anodes and Prussian blue analogue cathodes, showing the current progress in the development of ideal electrodes for sodium-ion batteries.

Keywords: Sodium-ion Battery, Hard Carbon, Prussian Blue Analogue, Initial Coulombic Efficiency, Energy Density

1. Introduction

Currently, Lithium-ion batteries (LIB) are the most common high-energy-density secondary batteries, powering countless devices, including phones, household appliances, and cars, and enabling society to operate efficiently. However, with increasing concern over the depletion of lithium on Earth, manufacturers have begun to consider alternatives to LIB. Currently, sodium-ion batteries (SIB) are considered the most promising counterpart. Compared to other alternative battery forms, SIBs, which utilize sodium that shares similar chemical properties with lithium, allow the replacement battery to be structurally and mechanistically identical to LIBs, enabling manufacturers to utilize their existing technologies to produce new batteries. In addition, the abundance of sodium on Earth also means that, unlike LIB, SIB is more sustainable and can be produced at a significantly lower cost. However, due to the larger ionic radius and mass of sodium atoms, SIB is intrinsically less energy-dense compared to their lithium counterpart, making them attractive in high-power load

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or size-limited applications, such as in cars or phones [1]. To overcome and minimize this performance discrepancy, various efforts have been made to enhance the electrochemical performance of sodium-ion batteries, particularly with improved electrode materials.

For the anode, hard carbon (HC) is considered one of the most promising materials for sodium-ion batteries. HC anode intercalates sodium ions within its nanopore structure, which is ideal in accommodating large ions and allows for high sodium-ion storage capacity and appropriate work potential, making it an ideal solution for effectively intercalating sodium ions with their large ionic radius [2]. For cathode, Prussian blue analogue (PBA) has attracted wide attention as a high redox potential, high volumetric capacity, and high structural stability material as it can be facilely synthesized from low-cost and non-toxic precursors and has a good balance in multiple electrochemical properties including specific capacity, cycle life, and rate performance compared to other cathode materials [3, 4]. In addition, the nanostructure of PBA creates a natural advantage in ion storage capacity per unit cell, reducing SIB's disadvantage in energy density.

Despite numerous advancements in the development of electrode materials, current reviews of SIB mainly focus on the general electrochemical performance and cost comparison to LIB while failing to address recent advancements in electrode performance that utilizes the nanostructure characteristics of materials. This may undermine some recent progress made in the electrochemical performance of the batteries and exaggerate the performance discrepancy between sodium and lithium-ion batteries. This paper aims to provide insight into the utilization of hard carbon anodes and Prussian blue analogue cathodes in sodium-ion batteries as well as characteristics in their nanostructure that allow further improvement of the material, thereby providing an accurate performance indication for this type of battery. The paper will begin by introducing hard carbon and Prussian blue, providing an overview of these materials and their advantages when used as electrode materials for sodium-ion batteries. It will then review current findings and experiments on hard carbon anodes and Prussian blue cathodes to compare their performance quantitatively with that of other materials through voltage-capacity curves, charge and discharge capacity, as well as initial coulombic efficiency (ICE), supporting their advantages in electrochemical performance.

2. Literature review

2.1. Hard carbon anodes: structure, storage sites, and rate-determining features

Hard carbon (HC) is distinctively different from graphite due to its orderless structure consisting of both short-range ordered domains similar to graphite interlayers and micropore domains. It is believed that the short-range domains are composed of curved graphene nanosheets with expanded interlayer spacing, where the micropore domains are located in between the short-range ordered domains. This characteristic allowed the existence of various Na^+ sites that cannot exist in graphite and makes HC ideal is a sodium ion storage material [5,6].

The Na^+ storage in HC is claimed to follow the "adsorption-filling" mechanism. The adsorption of sodium ions occurs at defect sites and open surfaces of HC and it normally accounts for 30% of overall capacity, while giving arise to a slope region between 1 and 0.1V. The filling of ions, on the other hand, occurs at the closed pore domains, where the filling of ions in quasi-metal state contributes to 70% of the capacity with a lower voltage plateau region below 0.1 V. Though the capacity ratio is claimed to be 30:70, HC shows strong precursor dependence on its carbon microstructure, meaning it has high structure tunability that can lead to significant differences in slope and plateau region capacities. In full battery applications, the slope region of HC can hinder the energy density and output voltage of SIBs, making it crucial to manipulate the precursor so the

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ordered-closed-pore domains are maximized, leading to a long and dominant low-voltage plateau region which is preferred for battery performance [7].

Currently, the universal approach to tune the microstructure of HC is through sintering. When HC is treated with high temperatures, the micro graphitic domains become more dominant as they become more long-range ordered, and the number of defects decreases, effectively reducing the slope region capacity. However, while sintering reduces the number of defects, it stimulates the growth of closed pore size, meaning that closed pores can be no longer optimal for ion storage due to weakened induced nucleation activity, limited Na^+ conductivity of high crystalline graphene walls, and low thermodynamic probability of quasi-metallic cluster formation, which are all significant once the closed pores grow oversize. This will result in a sharp decline of the plateau capacity, as well as the overall capacity, if sintering is done at a high temperature. As a result, compromises must be made as the current heat treatments of HC are set at moderate temperatures around 1400-1500 °C to balance the tradeoff between defects and closed pore size, maintaining considerable slope region capacity to avoid severe loss of plateau capacity. Alternatively, special precursors such as charcoal, bamboo, and wood rich in crystalline cellulose, which contain easy graphitizable components, have been screened out for plateau region dominated HC anodes. Chou et al. achieved an all-plateau and high-capacity topological graphitized carbon using corn cobs as the precursor, showing the potential of forming usable nanopores of appropriate sizes from such easily graphitizable components. To solve the constraint between graphitization enhancement and nanopore growth independent to precursor materials, Liu et al. designed modified flash Joule heating technology, producing metastable HC anodes from a kinetically controlled process instead of the thermodynamically controlled process in sintering processes. This process allows the graphitization degree and pore growth to be regulated by controlling the temperature and width of transient thermal pulses and allows the production of HC anodes with short-range ordered graphitic domains and appropriately sized nanopores. The metastable HC anodes show a significantly prolonged plateau region below 0.1V, with the best sample having 89.5% of overall capacity being plateau capacity at 325 mAh g^{-1}. In application, this HC anode allowed an increase of full battery energy dencity of up to 20.7% as tested with a $HC \,||\, Na_3V_2(PO_4)_3$ full battery [7].

Despite HC having excellent ion storage capability, its porous and orderless structure meant it had a high specific surface area, which leads to low initial coulombic efficiency (ICE) that hinders its electrochemical performance. While most research that aims to address these focuses on regulating the microstructure of HC material, research in developing the suitable binder for HC anode SIBs found materials that solve this challenge. The low ICE of HC anode is primarily a result of the formation of solid electrolyte interphase (SEI) layer, which can cause significant consumption of Na+ ions due to the high surface area of HC. If an artificial passivation film can be fabricated as a replacement to the SEI layer, the ion consumption can be reduced, and the ICE can be improved. Specifically, a trifunctional sodium alginate (SA)/polyethylene oxide (PEO) binder can be prepared through an esterification reaction, which generates a passivation film that inhibits the formation of SEI layer, reducing the irreversible loss of sodium ions and allowing a higher ICE up to 87% when coupled with glucose-derived carbon anode. In addition, the binder is universal appliable to different types of HC anodes [8].

2.2. Prussian blue analogue cathodes: lattice transport, redox tunability, and defect control

The structure of the Prussian Blue Analogues (PBAs) can be expressed as $M[Fe(CN)_6]_y \bullet zH_2O$ where A represents an alkali metal, M represents a transition metal, and $0 < x < 2$; $0 < y < 1$.

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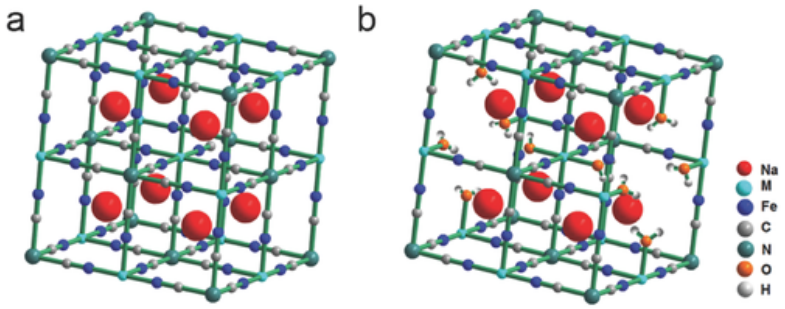


Figure 1. The PBA crystal framework. a) intact framework, b) defective framework with 25% $Fe(CN)_6$vacancies and interstitial water existing in each unit cell [9]

PBAs are considered ideal cathode materials for SIBs due to their easy transportation and accommodation of Na^+ ions. The crystal framework of PBA is illustrated in figure 1, where the sodium ions are stored in the interstitial sites within the crystal. The interstitial sites in PBA frameworks have a diameter of ≈4.6 angstrom, and the lattice structure has channels with diameter of ≈3.2 angstrom in the <100> direction. The size of the interstitial sites and channels allows easy transportation of the Na^+ ions and leads to a high diffusion coefficient of 10^{-9} to 10^{-8} cm^2 s^{-1} which is considerably higher comparing to conventional oxide phosphate cathodes, showing PBA's advantage in ionic conduction for SIBs [9].

However, the spacious PBA framework also made the material susceptible to structural defects, especially the effect of coupled interstitial water molecules as illustrated by structure b in figure 1. While studies from Hu et al. compared the cycling performance of low-vacancy Fe-PBAs with various amounts of interstitial water and concluded that water in PBA materials plays a critical role in stabilizing the framework, leading to PBAs with higher water content to exhibit better long-term cycling performance (HW-PB, containing the most water in the experiment, retained ≈91% capacity after 1380 cycles), it is generally agreed that interstitial water present within the PBA framework has a negative effect in the Na^+ diffusion rate by blocking the ion transportation, leading to inferior electrochemical performance. Song et al. demonstrated that by removing the interstitial water from $Na_2MnFe(CN)_6 \bullet zH_2O$, the electrochemical performance can be enhanced with a reversible discharge capacity of 150 mAh g^{-1}, and Ojwang et al. reported that thermal dehydrated low-defect Berlin Green (a PBA material) exhibited faster insertion and extraction of Na^+ with lower water content [10]. As most of the interstitial water molecules are incorporated to the material during synthesis, in a liquid-phase environment, during the generation of $[Fe(CN)_6]^{4-}$ vacancies in the framework that allowed water to be coupled, current research focused on reducing the growth rate of PBA in the synthesis process through introducing complexing agents which aims to reduce the concentration of free transition-metal cations and thus the number of vacancies [11].

Another unique advantage PBA electrode has over traditional transition metal or phosphate electrodes is that PBAs contain two redox active sites as both the iron and the transition metal can undergo complete electrochemical redox reactions and allowing 2 Na^+ to be inserted in each unit cell. This allows PBA compounds to have a higher theoretical capacity compared to traditional transition metal oxides (100-150 mAh g^{-1}) or phosphates (≈120 mAh g^{-1}), with examples like $Na_2FeFe(CN)_6$ having a theoretical capacity of ≈170 mAh g^{-1}, exceeding both [9]. In addition, PBA compounds are also ideal for their extra tunability. The iron atoms within the PBA framework can be substituted by other redox-active transition metals such as Co, Ni and Mn, resulting in different electrochemical responses. For example, $Na_2FeFe-PB$ has a charge plateau of around

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3.2 V, and substituting the iron in the structure to manganese will result in $Na_2MnFe-PBA$ which can elevate the voltage to 3.6 V [9].

2.3. Results and discussions

The orderless structure of HC gave it intrinsic closed pores and defect sites that allowed the intercalation of sodium ions. Effective capacity of HC anodes is in the plateau region with a low voltage below 0.1V and it originates from the filling of closed pore domains by sodium ions and takes up 70% of the total capacity. To increase the ratio of effective capacity without balancing the tradeoff between graphitization and closed pore size, or the dependency to certain precursors, flash Joule heating is used to produce metastable HC anodes with significantly prolonged plateau region below 0.1 V, taking up 89.5% of overall capacity [7]. HC intrinsically has a high specific surface area due to its porous and orderless structure, which leads to significant consumption of sodium ions in the formation of the SEI layer during the first charge cycle and leads to a low ICE. To improve its ICE, SA/PEO binder can be utilized as it can generate a passivation film on the anode which inhibits the formation of SEI layer, reducing the consumption of sodium ion and allowing a high ICE up to 87% [8].

PBA cathodes have ideal open frameworks that allow easy transportation of sodium ions, resulting in a high diffusion coefficient of 10^{-9} to 10^{-8} cm^2 s^{-1} [9]. However, PBA tends to form defects during synthesis which will couple to water molecules and negatively impact the ion transportation. Introduction of complexing agents in the synthesis process or dehydration through thermal processing both reduces the amount of interstitial water within the PBA framework, improving the electrochemical performance and allowing a higher reversible discharge capacity of 150 mAh g^{-1} in the case of $Na_2MnFe(CN)_6 \bullet zH_2O$. Despite the negative impact on electrochemical performance, the interstitial water has been proven to have a positive impact on its structural stability, leading to a good long-term cycling performance up to 91% after 1380 cycles [10,11]. The two redox sites (iron and transition metal) in PBA framework allow for high discharge capacity with $Na_2FeFe(CN)_6$ having a theoretical capacity of ≈170 mAh g^{-1}, edging over traditional metal oxide cathodes (100-150 mAh g^{-1}) or phosphate cathodes (≈120 mAh g^{-1}). The iron site can also be substituted by transition metal elements, leading to high potential tunability where $Na_2FeFe-PB$ has its charge plateau at 3.2 V and $Na_2MnFe-PBA$ has it at 3.6 V [9].

3. Conclusion

In conclusion, HC and PBA are both promising electrode materials that have advantages over traditional materials in SIBs. The orderless structure of HC allowed the formation of large ion intercalation sites that's impossible in ordered structures like graphite and made it suitable for sodium ion storage, and its structural tunability meant its efficiency can be artificially increased through heat treatment which leads to improvements in SIB electrochemical performance. PBA cathodes have large open frameworks that allow easy transportation of large sodium ions while also accommodating two substitutable redox sites per unit cell, leading to a natural advantage in capacity and tunability over traditional cathode materials. The materials also have natural disadvantages that have been addressed to some extent, making them promising in application. HC has a low ICE due to its high surface area, but it can be improved and made competitive with the use of SA/PEO binders in the electrode which reduces its disadvantage. On the other hand, there are various ways to control the interstitial water content in PBA cathodes, allowing the manufacturer to find the optimal balance between capacity and long-term cyclability.

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